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SUITABILITY OF 18 AROMATIC AMINES FOR OVERWATER STORAGE WHEN BLENDED WITH AVIATION GASOLINE

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MEMORANDUM REPORT

for the

Air Technical Service Command, Army Air Forces

SUITABILITY OF 18 AROMATIC AMINES FOR OVERWATER STORAGE WHEN BLENDED WITH AVIATION GASOLINE

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INTRODUCTION

As part of the general investigation of aromatic amines as antiknock additives for aviation fuels, requested by the Air Technical Service Command, Army Air Forces, the NACA Cleveland laboratory has been conducting a program to determine the suitability for overwater storage of fuel blends containing aromatic amines. The tests reported herein are a continuation of those reported in reference 1 and were completed in January 1945.

The overwater system for storing aviation fuel blends that contain additives such as amines results in loss of some of the additive to the water layer. An indication of the extent to which this loss can occur is conveniently expressed by the gasoline-water distribution coefficient, which is the ratio of additive concentration in the gasoline to that in the water layer at equilibrium. The significance of this coefficient and the method of experimentally determining it are given in detail in reference 1. Briefly, the coefficient is calculated from the following equation:

$$K_{wt} = \frac{W_r(W_w + W_e)}{W_e(W_g + W_r)}$$

where

K_{wt} gasoline-water distribution coefficient (weight basis)

W_r weight of amine remaining in gasoline phase at equilibrium

W_e weight of amine extracted by water phase at equilibrium

W_w weight of water

W_g weight of gasoline

The distribution coefficient calculated on a weight basis (concentrations expressed as grams of solute per gram of solution) may be converted to a volume basis (concentrations expressed as grams of solute per milliliter of solution) merely by multiplying by the specific gravity of the gasoline solution. It should be noted that this computed volume coefficient still pertains to the original weight concentration of amine in the fuel. The greater the distribution coefficient, the less will be the quantity of additive extracted by the water and, therefore, the more suitable the additive would be for overwater storage. Relations utilizing the distribution coefficient have been used for estimating the concentration of amine remaining in the gasoline as a function of the gasoline-water ratio by volume in an overwater-storage system. These relations are discussed in reference 2.

The overwater-storage suitability of 18 aromatic amines is discussed herein, and a substantiation of some of the postulates proposed in reference 1 concerning the correlation of gasoline-water distribution coefficients with molecular structure is included.

FUEL BLENDS, APPARATUS, AND PROCEDURE

The fuel used throughout this investigation (the same as that in reference 1) approximated the composition of typical current aviation fuel and permitted at the same time specific knowledge of the aromatic content. It consisted of an unleaded grade 65 gasoline from which the aromatic hydrocarbons had been extracted with 10-percent fuming sulfuric acid and silica gel to a concentration of less than 1 percent upon analysis. To this extracted gasoline was added a 15-percent (by volume) concentration of an aromatic hydrocarbon mixture composed of five parts xylene, two parts cumene, and one part toluene. The final test blends were prepared by adding 1,3, and 6 percent by weight of each amine to the previously described base stock.

The aromatic amines tested were synthesized and purified at the Cleveland laboratory with the exception of diphenylamine and N-methyl-diphenylamine, which were purchased and subsequently purified. The aromatic amines, together with their physical constants, are listed in table I; the properties serve as criterions of purity.

The apparatus and method of analysis are completely described in reference 1 and have not been altered in any way for the tests

reported herein. Equal weights of distilled water and amine solution are brought to equilibrium with each other at constant temperature. The water layer is separated and then analyzed for amines with a commercial spectrophotometer. Distribution coefficients reported herein were measured at 40° F and 100° F. A thorough discussion of the accuracy of the measurements made, including the various sources and magnitudes of the errors involved, is also presented in reference 1.

RESULTS AND DISCUSSION

Table II presents the experimentally determined values of gasoline-water distribution coefficients for 12 of the aromatic amines tested, arranged in order of increasing distribution coefficients using values for 3 percent concentration at 40° F, and therefore in order of increasing suitability for overwater storage. Distribution coefficients were not determined for six amines that were so insoluble in water that standard solutions for the analysis could not be prepared even in concentrations as low as 0.003 percent. In addition, all of these amines except diphenylamine have been found to be greater than 10 percent soluble in gasoline at -60° C. (See reference 3.) Such extreme insolubility in water coupled with correspondingly high solubility in gasoline assures high values for the distribution coefficients of these five amines. These amines would therefore be suitable for overwater storage.

The lowest distribution coefficients reported herein are for p- and o-ethylaniline, the coefficients of which are about the same as those of the xylidines. (See reference 1.) The amines listed below N-methyl-o-toluidine in table II can be used in blends stored over water with negligible loss if the last portion of the fuel is not withdrawn from the tank. Some further discussion of this problem has been presented in reference 1.

The observation made in reference 1, that for a given aromatic nucleus the addition of a $-CH_3$ group to N has a greater effect in increasing the distribution coefficient than adding $-CH_3$ to the ring or side chain, is further substantiated by the data reported herein. For example, beginning with o-toluidine (K = 6.24 for 3-percent blend at 40° F), the addition of a $-CH_3$ group to the side chain (o-ethylaniline) increases K to 20; whereas, addition of $-CH_3$ to N (N-methyl-o-toluidine) brings K up to 66. The same effect is shown in the case of the p-isomers. Similarly, beginning with 2,4-xylidine, the addition of a $-CH_3$ group to the ring (2,4,6-trimethylaniline) increases K from 20 to 82, whereas addition of a $-CH_3$ group to N (N-methyl-2,4-xylidine) brings K up to 165, a very pronounced effect in both cases. (Reference 1 includes K values for o- and p-toluidine, 2,4-xylidine, and 2,4,6-trimethylaniline.)

Also substantiated is the observation that increasing the number of carbon atoms in the aryl radical will increase the distribution coefficient.

SUMMARY OF RESULTS

Gasoline-water distribution coefficients were measured for 12 aromatic amines for three different concentrations at each of two temperatures. Distribution coefficients of six other amines were not obtained because of their insolubility in water. The aromatic amines studied may be tabulated in the approximate order of decreasing suitability for overwater storage of their blends as follows:

N-Methyl-diphenylamine
Diphenylamine
N,N-Dimethyl-2-methyl-5-isopropylaniline
N,N-Dimethyl-2,4,6-trimethylaniline
N-Isopropyl-*p*-isopropylaniline
N-Methyl-*p*-*tert*-butylaniline
N-Methyl-*p*-isopropylaniline
N-Methyl-*p*-ethylaniline
N-Methyl-*ar*-ethylanilines
N-Methyl-2,4-xylidine
N-Methylcumidines
N-Methylxylidines
N-Methyl-*o*-toluidine
o-Isopropylaniline
N-Methyltoluidines (80 percent *p*-, 20 percent *o*-)
N-Methyltoluidines (60 percent *p*-, 40 percent *o*-)
o-Ethylaniline
p-Ethylaniline

The following correlations were noted in the present investigation:

(a) For a given aromatic nucleus, adding $-CH_3$ to N has a greater effect in increasing overwater-storage suitability than adding $-CH_3$ to the ring or to a side chain.

(b) Increasing the number of carbon atoms in the aryl radical increases the overwater-storage suitability.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 20, 1945.

REFERENCES

1. Olson, Walter T., Tischler, Adelbert O., and Goodman, Irving A.: Gasoline-Water Distribution Coefficients of 27 Aromatic Amines. NACA Memo. rep., Aug. 3, 1944.

2. Olson, Walter T., and Tischler, Adelbert O.: Loss of Xylidines in Overwater Storage of Xylidine-Blended Fuel. NACA Memo. rep., March 18, 1944.

3. Kelly, Richard L.: The Low-Temperature Solubility of 24 Aromatic Amines in Aviation Gasoline. NACA MR No. E4K17, Nov. 17, 1944.

TABLE I - AROMATIC AMINES AND THEIR PHYSICAL PROPERTIES

Amine	Boiling range at 760 mm (°C)	Refractive index n_D^{20}	Density at 20° C (grams/ml)
o-Ethylaniline	211	1.5602	0.9810
p-Ethylaniline	216	1.5547	.9672
o-Isopropylaniline	219-220	1.5484	.9643
N-Methyltoluidines (60% *p*-, 40% *o*-)	208.5-215	1.5600	.9668
N-Methyltoluidines (80% *p*-, 20% *o*-)	210-213	1.5590	.9638
N-Methyl-*o*-toluidine	206.5-207.5	1.5646	.9763
N-Methyl-*p*-ethylaniline	227.5	1.5485	.9485
N-Methyl-*ar*-ethylanilines	222.5-230.5	1.5493	.9503
N-Methyl-*p*-isopropylaniline	240	1.5390	.9347
N-Methyl-2,4-xylidine	221-222	1.5542	.9582
N-Methylcumidines	237.5-241.5	1.5390	.9366
N-Methylxylidines	220-227	1.5540	.9586
N-Methyl-*p*-*tert*-butylaniline	246.5-249.5	1.5348	.9305
N-Isopropyl-*p*-isopropylaniline	246-247	1.5209	.9075
N,N-Dimethyl-2-methyl-5-isopropylaniline	[a]84	1.5124	.9028
N,N-Dimethyl-2,4,6-trimethylaniline	213.5	1.5116	.9066
Diphenylamine	[b]52.9-53.6	----------	----------
N-Methyl-diphenylamine	295-296	1.6224	1.0527

[a]Distilled under reduced pressure (5 mm).
[b]Melting point instead of boiling range was measured for this solid.

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TABLE II - DISTRIBUTION COEFFICIENTS OF AROMATIC AMINES TESTED

Amine	Original concentration in fuel (percent by weight)	40° F: Concentration in water at equilibrium (percent by weight)	40° F: Distribution coefficient on weight basis K_{wt}	40° F: Distribution coefficient on volume basis[a,c] K_{vol}	100° F: Concentration in water at equilibrium (percent by weight)	100° F: Distribution coefficient on weight basis K_{wt}	100° F: Distribution coefficient on volume basis[b,c] K_{vol}
p-Ethylaniline	1	0.067	14	10	0.040	24	17
	3	.171	17	12	.105	28	20
	6	.288	20	15	.180	33	23
o-Ethylaniline	1	0.054	16	13	0.032	30	21
	3	.146	20	15	.088	33	23
	6	.244	24	18	.152	39	27
N-Methyltoluidines (60% *p*-, 40% *o*-)	1	0.029	34	25	0.020	49	35
	3	.074	40	29	.051	58	41
	6	.129	46	34	.091	65	46
N-Methyltoluidines (80% *p*-, 20% *o*-)	1	0.022	45	33	0.015	65	46
	3	.053	56	41	.038	79	56
	6	.091	65	48	.064	93	65
o-Isopropylaniline	1	0.021	47	34	0.010	100	70
	3	.053	56	41	.030	100	70
	6	.090	66	48	.053	115	80
N-Methyl-*o*-toluidine	1	0.021	47	34	0.011	94	66
	3	.045	66	48	.029	105	74
	6	.078	76	56	.051	115	80
N-Methylxylidines	1	0.010	100	73	0.005	200	140
	3	.021	140	105	.013	230	160
	6	.039	150	110	.024	250	175
N-Methylcumidines	1	0.009	110	81	0.003	300	210
	3	.020	150	110	.010	300	210
	6	.035	170	125	.019	320	230
N-Methyl-2,4-xylidine	1	0.009	110	81	0.005	200	140
	3	.018	165	120	.012	250	175
	6	.028	210	155	.017	350	250
N-Methyl-*ar*-ethylanilines	1	0.006	155	115	0.005	200	140
	3	.017	180	130	.011	270	190
	6	.030	200	145	.025	240	170
N-Methyl-*p*-ethylaniline	1	0.006	160	115	0.003	300	210
	3	.015	200	145	.010	300	210
	6	.028	210	155	.018	330	230
N-Methyl-*p*-isopropylaniline	1	0.003	300	220	0.001	1000	700
	3	.006	500	370	.004	800	550
	6	.009	700	500	.008	800	550
N-Methyl-*p*-*tert*-butylaniline N-Isopropyl-*p*-isopropylaniline N,N-Dimethyl-2-methyl-5-isopropylaniline N,N-Dimethyl-2,4,6-trimethylaniline Diphenylamine N-Methyl-diphenylamine	Standard water solutions of these amines could not be prepared because of the very low water solubility of the amine.						

[a]Density of gasoline solution at 40° F, 0.732 gram/ml.
[b]Density of gasoline solution at 100° F, 0.704 gram/ml.
[c]Values for K_{vol} were computed by multiplying the corresponding K_{wt} values by the density of the gasoline solution.

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